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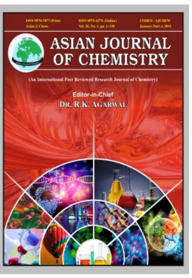

Structural Investigation on Pharmaceutical Intermediate *o*-Chlorobenzoyl Chloride: A DFT Approach

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The FT-IR and FT-Raman spectra of *o*-chlorobenzoyl chloride were recorded in the regions 4000-400 cm^{-1} and 3500-100 cm^{-1}. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) and standard B3LYP/6-311+G** basis set combination. The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical (SQM) force field. The infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. Further, density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

Keywords: Vibrational spectra, FT-IR and FT-Raman spectra, DFT calculation, First-order hyperpolarizability.

INTRODUCTION

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra[1,2]. A significant advancement in this area was made by combining semi empirical quantum mechanical method; *ab initio* quantum mechanical method and density functional theory (DFT), each method having its own advantage[3-6]. In scaled quantum mechanical (SQM) approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules[2,7,8] and were recommended for general use. In the present investigation, the vibrational analysis of *o*-chlorobenzoyl chloride using the SQM force field method based on DFT calculation was presented. The infrared and Raman spectra of the *o*-chlorobenzoyl chloride were also simulated utilizing the computed dipole derivatives for IR and polarizability derivatives for Raman activities. Further, we adopted density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

EXPERIMENTAL

Spectroscopically pure *o*-chlorobenzoyl chloride was obtained from Lancaster chemical company, U.K. and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of *o*-chlorobenzoyl chloride was recorded in the 4000-400 cm^{-1} region at a resolution of ± 1 cm^{-1}, using BRUKER IFS-66V vacuum Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum was recorded on the same instrument with FRA-106 Raman accessories in the region 3500-100 cm^{-1}. Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

Computational details: In order to find the most optimized molecular geometry, the energy and vibrational frequency calculations were carried out for *o*-chlorobenzoyl chloride with GAUSSIAN 98W software package[9] using the B3LYP functional[10,11] standard 6-311 + G** (large) basis sets. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure[12,13] using selective scaling in the natural internal coordinate representation[14,15]. Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scale factors, calculation of the total energy distribution (TED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program (version 7.0-G77) written by Sundius[16,17,18]. For the plots of simulated IR and Raman spectra, pure Lorentizian band shapes were used with a band width of 10 cm^{-1}.

The symmetry of the molecule was also helpful in making vibrational assignments. By combining the results of the GAUSSVIEW program[19] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. The defined local symmetry coordinates[20-23] form complete set and matches quite well with the motions observed using the GAUSSVIEW program[19].

RESULTS AND DISCUSSION

Molecular geometry: The optimized molecular structure of *o*-chlorobenzoyl chloride was shown in Fig. 1. The global minimum energy obtained by the DFT structure optimization was presented in Table-1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table-2.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 48 standard internal coordinates containing 12 redundancies were defined as given in Table-3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi *et. al*[5,6,14,15] are summarized in Table-4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

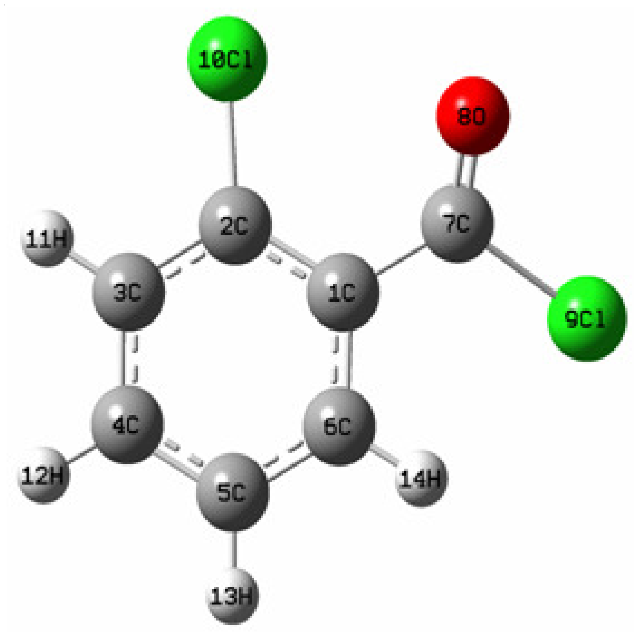

Fig. 1. The optimized molecular structure of *o*-chlorobenzoyl chloride

TABLE-1
TOTAL ENERGIES OF *o*-CHLOROBENZOYL CHLORIDE CALCULATED AT DFT (B3LYP)/6-31G* AND (B3LYP)/6-311 + G** LEVEL

Method	Energies (Hartrees)
6-31G*	-1264.54843900
6-311 + G**	-1264.76957264

Analysis of vibrational spectra: The 36 normal modes of *o*-chlorobenzoyl chloride are distributed among the symmetry species as $\Gamma_{3N-6} = 25\,A'$ (in-plane) + $11\,A''$ (out-of-plane) and in agreement with C_s symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A″) to depolarized band.

The detailed vibrational assignments of fundamental modes of *o*-chlorobenzoyl chloride along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were reported in Table-5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of *o*-chlorobenzoyl chloride are produced in a common frequency scales in Fig. 2 and 3.

Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$\text{RMS} = \sqrt{\frac{1}{n-1}\sum_{i}^{n}(\nu_i^{\text{calc}} - \nu_i^{\text{exp}})^2}$$

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311 + G**) of *o*-chlorobenzoyl chloride was found to be 109 cm^{-1}. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and

TABLE-2
OPTIMIZED GEOMETRICAL PARAMETERS OF *o*-CHLOROBENZOYL CHLORIDE OBTAINED BY B3LYP/ 6–311 + G** DENSITY FUNCTIONAL CALCULATIONS

Bond length	Value (Å)	Bond angle	Value (Å)	Dihedral angle	Value (Å)
C2-C1	1.41414	C3-C2-C1	120.3423	C4-C3-C2-C1	0.98560
C3-C2	1.39565	C4-C3-C2	120.34093	C5-C4-C3-C2	-0.65574
C4-C3	1.39287	C5-C4-C3	120.12402	C6-C5-C4-C3	-0.29085
C5-C4	1.39512	C6-C5-C4	119.62347	C7-C1-C6-C5	177.02637
C6-C5	1.38942	C7-C1-C6	120.69086	O8-C7-C1-C6	-155.47786
C7-C1	1.48656	O8-C7-C1	127.66669	Cl9-C7-C1-C6	24.83177
O8-C7	1.18951	Cl9-C7-C1	114.17689	Cl10-C2-C1-C6	-178.44100
Cl9-C7	1.84426	Cl10-C2-C1	122.98120	H11-C3-C2-C1	-179.02943
Cl10-C2	1.74763	H11-C3-C2	118.93682	H12-C4-C3-C2	179.56864
H11-C3	1.08446	H12-C4-C3	119.43315	H13-C5-C4-C3	179.97229
H12-C4	1.08623	H13-C5-C4	120.56340	H14-C6-C5-C4	-179.71471
H13-C5	1.08540	H14-C6-C5	119.93207	–	–
H14-C6	1.08284	–	–	–	–

*for numbering of atom refer Fig. 1

TABLE-3
DEFINITION OF INTERNAL COORDINATES OF *o*-CHLOROBENZOYL CHLORIDE

No (i)	Symbol	Type	Definition
Streching 1-4	r_i	C-H (arom.)	C3-H11, C4-H12, C5-H13, C6-H14
5	R_i	C-Cl (arom.)	C2-Cl10
6	R_i	C-Cl (sub.)	C7-Cl9
7	p_i	C-O (sub.)	C7-O8
8-13	P_i	C-C (ring)	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
14	P_i	C-C (sub.)	C7-C1
Bending 15-22	θ_i	C-C-H	C2-C3-H11, C4-C3-H11, C3-C4-H12, C5-C4-H12, C4-C5-H13, C6-C5-H13, C5-C6-H14, C1-C6-H14
23	β_i	C-C-Cl	C1-C7-Cl9
24-25	β_i	C-C-Cl	C1-C2-Cl10,C3-C2-Cl10
26	γ_i	C-C-O	C1-C7-O8
27-28	α_i	C-C-C	C6-C1-C7, C2-C1-C7
29-34	α_i	C-C-C (ring)	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
Out-of-plane 35-38	ω_i	C-H	H11-C3-C2-C4, H12-C4-C3-C5, H13-C5-C4-C6, H14-C6-C5-C1
39	ω_i	C-Cl	Cl10-C2-C1-C3
40	ω_i	C-C	C7-C1-C2-C6
41	ω_i	C-Cl	C1-C7-O8-Cl9
Torison 42-47	τ_i	τring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3
48	τ_i	τC-Cl	C2(C6)-C1-C7-O8(Cl9)

*for numbering of atom refer Fig. 1

TABLE-4
DEFINITION OF LOCAL SYMMETRY COORDINATES AND THE VALUE CORRESPONDING SCALE FACTORS USED TO CORRECT THE FORCE FIELDS FOR *o*-CHLOROBENZOYL CHLORIDE

No.(i)	Symbol[a]	Definition[b]	Scale factors used in calculation
1-4	C-H	r1, r2, r3, r4	0.920
5	C-Cl (arom.)	R5	0.927
6	C-Cl (sub.)	R6	0.927
7	C-O	p7	0.918
8-13	C-C	P8, P9, P10, P11, P12, P13	0.902
14	C-C (sub.)	P14	0.902
15-18	C-C-H	(θ15 - θ16) /√2, (θ17 - θ18) /√2, (θ19 - θ20) /√2, (θ21 - θ22) /√2	0.942
19	C-C-Cl	β23	0.947
20	C-C-Cl	(β24 - β25) /√2	0.947
21	C-C-O	γ26	0.979
22	C-C-C	(α27 - α28) /√2	0.986
23	b ring	(α29 - α30 + α31 - α32 + α33 - α34)/√6	0.986
24	b ring	(2α29 - α30 - α31+ 2α32 - α33 - α34)/√12	0.986
25	b ring	(α30 - α31 + α33 - α34)/2	0.986
26	C-H	ω35, ω36, ω37, ω38	0.963
27-30	C-Cl	ω39	0.965
31	C-C	ω40	0.935
32	C-Cl	ω41	0.963
33	t ring	(τ42 - τ43 + τ44 - τ45 + τ46 - τ47)/√6	0.935
34	t ring	(τ42 - τ44 + τ45 - τ47)/2	0.935
35	t ring	(-τ42 + 2τ43 - τ44 - τ45 + 2τ46 - τ47)/√12	0.935
36	τ C-Cl	τ48/4	0.945

[a] These symbols are used for description of the normal modes by TED in Table-5

[b] The internal coordinates used here are defined in Table-3

partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 9 cm^{-1} between the experimental and scaled frequencies of the *o*-chlorobenzoyl chloride.

TABLE-5
DETAILED ASSIGNMENTS OF FUNDAMENTAL VIBRATIONS OF *o*-CHLOROBENZOYL CHLORIDE BY NORMAL MODE ANALYSIS BASED ON SQM FORCE FIELD CALCULATION

No.	Symmetry species Cs	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1}) with B3LYP/6-311+G ** force field				TED (%) among type of internal coordinates[c]
		Infrared	Raman	Un scaled	Scaled	IR[a] A_i	Raman[b] I_i	
1	A'	3113 w		3162	3117	0.133	67.02	CH(99)
2	A'	3097 w	3082 s	3254	3095	0.103	91.11	CH(99)
3	A'	3074 vw		3213	3070	0.345	22.70	CH(99)
4	A'	3026 vw		3194	3028	0.307	81.88	CH(99)
5	A'	1942 w		2145	1947	0.732	76.02	CO(47), gClO(18), CC(12), tCCl(7), bCCl(5)
6	A'	1786 vs	1790 s	1992	1791	0.127	63.50	CO(68), bCH(18), bring(12)
7	A'	1638 s		1936	1641	0.937	23.18	CC(68), bCH(16), bring(11)
8	A″	1588 w	1592 vs	1803	1601	0.796	1.599	CC(50), bCH(44)
9	A'	1568 s	1574 s	1773	1572	0.39	16.26	CC(52), bCH(35), bCC(8)
10	A″	1463 s		1623	1467	0.654	3.34	CC(89)
11	A'	1439 s		1672	1442	0.486	16.42	bCH(66), CC(19), bCC(8)
12	A″	1348 w		1536	1352	0.373	14.98	CC(56), bring(26), bCH(12)
13	A'	1287 vs		1514	1292	0.324	17.87	bCH(86), CC(13)
14	A″	1267 s		1472	1271	0.207	6.41	CC(41), bCH(38), CCl(9), bCC(8)
15	A″	1192 s	1196 s	1388	1196	0.028	5.19	bring(47), CC(23), CCl(17), bCH(10)
16	A'	1166 s	1171 s	1377	1169	0.082	7.43	bring(77), bCH(19)
17	A'	1138 s	1142 s	1342	1142	0.723	4.28	tring(83), gCH(16)
18	A'	1067 s		1317	1069	0.558	8.39	tring(81), gCH(11), gCC(5)
19	A'	1043 s	1047 s	1243	1046	0.744	1.14	tring(70), CO(6), gCC(6), gCH(6)
20	A″	957 vs		1047	959	0.155	6.99	b ring(21), CC(21), bCO(14), gClO(14), gCH(7), CCl(6)
21	A″	866 s		1038	870	0.996	6.11	gCH(50), gCC(24), tring(11), bCO(6), bCCl(5)
22	A″	766 s		921	768	0.06	0.86	gCCl(26), gCC(24), bring(12), bCO(9), gCH(7), tring(7)
23	A'	726 s		942	729	0.03	3.54	gCCl(31), gCC(19), bring(10), gCH(9), tring(9), ClO(6)
24	A'	707 s		901	711	0.351	11.43	gCCl(36), gClO(27), bring(9), bCC(6)
25	A'	668 s	664 s	872	671	0.147	0.62	bCCl(23), CO(18), gClO(18), bCO(13), tring(6), gCH(5)
26	A″	642 s	647 w	832	647	0.86	1.16	bCCl(20), tring(11), CC(11), gCC(10), gClO(8), bCC(8)
27	A'		545 s	743	548	0.79	5.65	tring(38), gCCl(25), gCH(9), CO(7), tCCl(6)
28	A'		486 s	646	491	0.68	6.44	tring(43), tCCl(23), gCC(16), CO(7)
29	A″	460 s	451 s	620	464	0.291	0.18	tCCl(38), CCl(16), gClO(11), bring(10), gCH(10)
30	A″	440 s		598	445	0.143	0.12	bCCl(28), tring(16), CO(13), bCC(10), gClO(7)
31	A'		431 s	586	436	0.876	4.78	tCCl(18), CO(16), bCCl(12), bCO(12), bring(12), CC(10)
32	A'		363 w	547	367	0.10	1.36	bCCl(42), CO(12), gCC(10), gCCl(9), tring(7)
33	A'		260 s	428	266	0.103	2.43	CO(34), gCC(24), gCCl(14), tring(13)
34	A'		247 s	412	253	0.141	0.53	CO(47), bCCl(18), bCC(14), gClO(10)
35	A'		173 w	363	177	0.129	3.03	tring(33), CCl(21), CO(15), gCC(12), tCCl(11)
36	A'		141 w	244	145	0.35	0.28	tCCl(40), CO(37), CCl(16)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; *vs*, very strong; w, weak; vw, very weak

[a] Relative absorption intensities normalized with highest peak absorption

[b] Relative Raman intensities calculated by Eqn.1 and normalized to 100

[c] For the notations used see Table-4

C-C vibrations: The bands between 1650-1480 cm^{-1} are assigned to C-C stretching modes[23]. In the present study, the carbon stretching vibrations of the *o*-chlorobenzoyl chloride have been observed at 1638, 1588, 1568 cm^{-1} in the FT-IR and 1592, 1574 cm^{-1} in FT-Raman spectrum and are presented in Table-5. These assignments are in good agreement with literature[24,25].

C-H vibrations: Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm^{-1} due to aromatic C-H stretching vibrations. The bands due to C-H in-plane ring bending vibration interacting with C-C stretching vibration are observed as a number of m-w intensity sharp bands in the region 1300-1000 cm^{-1}. C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900-667 cm^{-1}[26]. Accordingly, in the present study the C-H vibrations of the title compounds are observed at 3097, 3074, 3026 cm^{-1} in the FT-IR spectrum and 3082 in FT-Raman for *o*-chlorobenzoyl chloride.

C-Cl vibrations: C-Cl vibrations are found in the region below 1000 cm^{-1}. The C-Cl stretching frequency is generally observed in the region 800-600 cm^{-1} depending on the configuration and conformation of the compound [27-28]. Based on this, the FT-IR bands at 766, 726, 707, 668, 642 cm^{-1} and FT-Raman bands at 664, 647 cm^{-1} have been assigned to C-Cl stretching in *o*-chlorobenzoyl chloride.

C-O vibrations: The carbonyl stretching generally occurs as a strong absorption in the region from 1730 to 1645 cm^{-1}. This portion of the infrared spectrum is most useful because the position of the carbonyl absorption is quite sensitive to substitution effects and the geometry of the molecule. Accordingly,

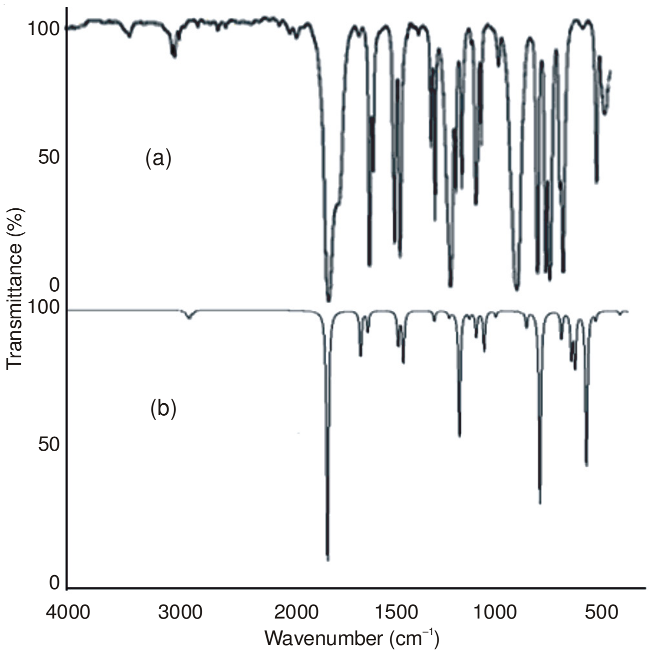

Fig. 2. FT-IR spectra of *o*-chlorobenzoyl chloride (a) observed (b) calculated with B3LYP/6-311+G**

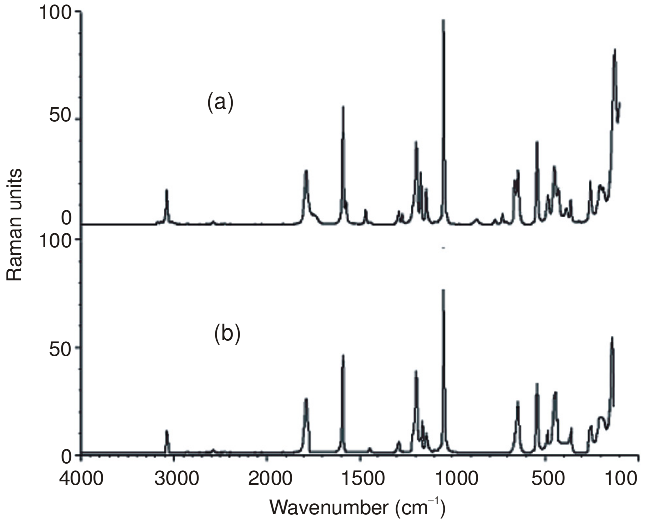

Fig. 3. FT-Raman spectra of *o*-chlorobenzoyl chloride (a) observed (b) calculated with B3LYP/6-311+G**

in the present investigation, the peaks identified at 1790 and 1786 cm^{-1} have been assigned to C=O stretching vibrations for *o*-chlorobenzoyl chloride.

Ring vibrations: Many ring modes are affected by the substitution in the aromatic ring. In the present study, the bands absorbed at 1192, 1166, 1138, 1067, 1043, 957, 866 cm^{-1} and 486, 440 cm^{-1} have been designated to ring in-plane and out-of-plane bending modes, respectively.

Hyperpolarizability calculations: The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of *o*-chlorobenzoyl chloride is calculated using 3-21 G (d,p) basis set based on finite field approach. Hyperpolarizability is a third rank tensor that can be described by a 3 × 3 × 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry[29]. The calculated first-order hyperpolarizability (btotal) of *o*-chlorobenzoyl chloride is 1.289537 × 10^{-30} esu, which is nearly seven times that of urea (0.1947 × 10^{-30} esu). The calculated dipole moment (μ) and first-order hyperpolarizibility (β) are shown in Table-6.

TABLE-6
THE DIPOLE MOMENT (μ) AND FIRST-ORDER HYPERPOLARIZIBILITY (β) OF *o*-CHLOROBENZOYL CHLORIDE DERIVED FROM DFT CALCULATIONS

β_{xxx}	24.6798306
β_{xxy}	4.1106034
β_{xyy}	2.7371947
β_{yyy}	-3.5868028
β_{zxx}	-118.5181275
β_{xyz}	-0.7739399
β_{zyy}	1.3003588
β_{xzz}	-12.4290667
β_{yzz}	5.030306
β_{zzz}	-36.030306
β_{total}	1.289537
μ_x	2.1196756
μ_y	0.0228399
μ_z	0.570441
μ	2.195211

Dipole moment (μ) in Debye, hyperpolarizibility β(-2ω;ω,ω) 10^{-30}esu

Conclusion

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311 + G** level have been carried out to analyze the vibrational frequencies of *o*-chlorobenzoyl chloride. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 9 cm^{-1} between the experimental and scaled frequencies. This close agreement established between the experimental and scaled frequ-encies obtained using large basis set (6-311 + G**) calculations has proved to be more reliable and accurate than the calculations using lower basis sets. The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of *o*-chlorobenzoyl chloride is calculated using 3-21 G (d,p) basis set based on finite field approach. The calculated first-order hyperpolarizability (β_{total}) of *o*-chlorobenzoyl chloride is 1.289537 × 10^{-30} esu, which is nearly seven times that of urea (0.1947 × 10^{-30} esu).

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